

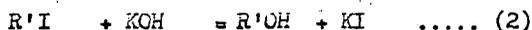
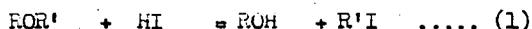
ETHER OXYGEN IN COAL

J. N. Bhaumik, A. K. Mukherjee, P.N. Mukherjee  
and A.Lahiri

Central Fuel Research Institute, P.O.Jealgora,  
Dhanbad, India

Recent work<sup>1</sup> on the state of oxygen in coal structure has established that the major part of oxygen occurs in the form of functional groups, such as -COOH, -OH and >CO. However, a substantial percentage of oxygen, is believed to be present probably as ether or in heterocyclic combination particularly in high rank coals, although direct experimental confirmation is lacking. In the present paper an account is given of the investigations that have been carried out to elucidate the state of oxygen in such combinations.

Treatment of coal with hydriodic acid at an elevated temperature should result in the break-down of ether structure and the ether oxygen will appear as -OH groups. In case of aryl ethers the -OH groups formed on HI treatment will be a direct measure of the ether oxygen. But if mixed ethers are present, the alkali hydrolysis of the HI treated product will result in the formation of further quantity of -OH groups. Therefore the estimation of -OH groups in two stages, as stated above, will give a quantitative measure of the different types of ether oxygen in coal. The course of reaction may be presented as follows :



The above method has been applied to estimate the ether oxygen present in coal. However, it is well-known that in case of unsaturation, the treatment with HI will lead to the addition of hydrogen and iodine to the unsaturated carbon atoms. The iodine thus combined will undergo alkali hydrolysis with the formation of hydroxyl groups. Thus it appears that on the basis of HI treatment and subsequent hydrolysis alone it is not possible to obtain unequivocal evidence regarding the presence of mixed ether in complicated structures like coal, which is likely to contain unsaturation in its structure. To eliminate this uncertainty, unsaturation in coal was estimated by the method developed by the authors earlier<sup>2</sup>.

Experimental

In the present experiments, vitrains from different ranks of coal were selected. The samples were refluxed with hydriodic acid ( 8 c.c. of HI per gm. of coal, sp. gr. of HI = 1.7) for a period of 8 hours at 130°C and then washed free of hydriodic acid. The product was subsequently analysed for hydroxyl groups.

Estimation of "-OH" groups :- About 1 gm. of the sample was accurately weighed and acetylated with acetic anhydride (20 c.c.) and fused sodium acetate (15 gm.) (by refluxing for 3.5 hours at 140°C. The acetylated product was washed free from acids and hydrolysed by 20 p.c. KOH solution. The product was next acidified with concentrated sulphuric acid and the acetic acid liberated was distilled off and titrated against standard

(see over)

alkali. The p.c. of oxygen as -OH in the HI treated samples was calculated on the initial coal basis.

A second part of the HI treated sample was hydrolysed by aqueous KOH (2.5 N) solution under reflux. The product thus obtained was acidified by hydrochloric acid, washed free of chlorides, and the "-OH" content was subsequently estimated by the above method.

The functional oxygen groups in vitrains were estimated by the conventional methods. The carboxyl and the carbonyl groups in the vitrains were found to remain unaffected by HI-treatment.

For the estimation of unsaturation in coal, oxidation by potash permanganate in dilute aqueous solution was employed. It is known that  $KMnO_4$  in dilute aqueous solution brings about hydroxylation of ethylenic double bonds, provided that the reaction is not carried too far and the temperature does not exceed 0°C. The reaction is best carried out in neutral medium. Two hydroxyl groups are formed per one unsaturation linkage.

TABLE - I

Coals	% C	% H	% N	% S	% O (By difference)
A	79.4	5.6	1.9	0.6	12.5
B	83.0	5.8	2.3	0.5	8.4
C	88.0	5.2	2.3	0.5	4.0

TABLE - II

Coals	Total Oxygen %	-OH Oxygen %	-CO- Oxygen %	-COOH Oxygen %	Total reactive Oxygen %	Unaccounted for Oxygen %
A	12.5	6.0	1.6	0.8	8.4	4.1
B	8.4	4.2	0.5	0.2	4.9	3.5
C	4.0	1.2	0.2	0.0	1.4	2.6

TABLE - III

Distribution of ether oxygen in vitrains  
(expressed on initial d.a.f. coal basis)

Coal	Total unreactive oxygen %	Increase in % oxygen as -OH after HI-treatment	Increase in % oxygen as -OH on subsequent hydrolysis	P.C. Oxygen as ether	P.C. of unreactive oxygen as ether
A	4.1	2.3	2.9	2.3	56.1
B	3.5	2.2	Nil	2.2	62.8
C	2.6	1.6	Nil	1.6	61.5

(see over)

TABLE - IV

Increase in oxygen p.c. as -OH on permanganate (d.a.f. coal basis) oxidation

Coals	Increase in p.c. oxygen as -OH after $KMnO_4$ oxidation
A	2.1
B	Nil
C	Nil

### Results and Discussion

The elemental composition as well as the distribution of oxygen in different functional groups of the vitrain samples is presented in Tables I and II. The increase in hydroxyl contents after HI treatment as well as after subsequent alkali - hydrolysis is shown in Table III. It was stated earlier that the increase in OH groups after HI - treatment is to be attributed to the ether linkages, and as such, the increase in oxygen p.c. as "-OH" gives a direct measure of ether oxygen present in coal. In case of mixed ether, however, the alkali hydrolysis of the HI treated product will lead to the formation of additional amount of "-OH" groups.

From an inspection of the Table III it is evident that coals of high rank (B & C) contain only aryl ethers and the increase in oxygen p.c. as "-OH" directly measures the percentage of ether oxygen. In case of low rank coal (A), however, the formation of a significant amount of hydroxyl groups on alkaline hydrolysis probably indicates the presence of mixed ethers. Assuming that the hydrolysis step of the iodo-derivative goes to completion, the increase in -OH contents on alkaline hydrolysis should be equal to that obtained on HI-treatment. The apparent discrepancy between the two values, as evident from Table III, may therefore be ascribed either to experimental errors or to some complicating factor. From Table IV it will be seen that unsaturation occurs in coal of this particular rank. The addition of HI to the double bonds leads to the formation of -OH groups on subsequent hydrolysis. It appears, therefore, that for coals of low rank, the formation of -OH groups on hydrolysis of the HI treated product is partly due to the presence of unsaturation. Thus, for low rank coals, the apparent lack of agreement between the values of hydroxyl groups may be largely explained in terms of unsaturation. It may therefore be concluded that a significant percentage of ether oxygen is present in coals of different rank and that the low rank coals are characterised by the presence of mixed ethers. It would appear that about 60 p.c. of the total unreactive oxygen in coals of different ranks are present in ether combination.

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